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FUNGICIDAL TESTS ON BLUE MOLD (PERONOSPORA TABACINA) OF TOBACCO[1]

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INTRODUCTION

In 1938 Clayton et al. (*1*, *2*)[2] reported a copper oxide-cottonseed oil spray treatment for the control of the blue mold (*Peronospora tabacina* Adam) disease of tobacco (*Nicotiana tabacum* L.). It was demonstrated that this spray treatment reduced disease development to such a degree that even under severe conditions measurable damage was prevented; i. e., there was no appreciable retardation of plant growth or reduction in the number of plants produced. Since 1938 these findings have been repeatedly verified, and the treatment has been used extensively by tobacco growers. The problem of spray control for blue mold, however, has been of great interest not only because of the practical control afforded but also because of the ques tions raised as to the nature of the protection that the spray provides.

As reported previously, bordeaux mixture is not effective against blue mold, nor is copper oxide effective when used alone. However, copper oxide when combined with cottonseed oil gives good control of the disease. The oil, as will be shown later, contributes the chief disease-control value of the mixture. While mineral oils are used extensively in present-day spray practice as insecticides, and to a limited degree with copper fungicides as spreaders and stickers, the vegetable or glyceride oils have been used very little. They are somewhat more expensive than the mineral oils, and not so readily emulsified. However, the glyceride oils have been shown to possess both insecticidal and fungicidal value; they are essentially mixtures of the glycerides of various fatty acids, and Siegler and Popenoe (*14*) have demonstrated that caproic and lauric acids are efficient contact insecticides. Martin and Salmon (*12*) in 1933 reported that a number of vegetable oils were fungicidal against the hop powdery mildew. The first objective of the present investigation, consequently, was to discover more of the fungicidal possibilities of the vegetable oils. Certain animal and mineral oils, as well as nonglyceride oils of vegetable origin, were included in some experiments for purposes of comparison. Since the word "fungicidal" has had broad as well as restricted usage, it is well to mention here that in the following discussion the term "fungicidal" refers to either destruction of the fungus or inhibition of fungal growth. No attempt has been made to distinguish between fungicidal and fungistatic action. Inhibition of

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[2] Italic numbers in parentheses refer to Literature Cited, p. 275.

growth was soon followed by the death of the tobacco blue mold (downy mildew) fungus.

METHODS OF STUDY

Blue mold has proved a very convenient disease with which to conduct fungicidal investigations. It attacks the plants as seedlings, and greenhouse conditions during the late fall, winter, and early spring months are most favorable for its development. The usual procedure has been to sow tobacco seed in 6-inch pots, and thin to a uniform stand. After the pots had received 3 to 4 applications of spray, they were inoculated with a spore suspension and placed under conditions favorable for disease development. Sprays were applied twice weekly for a total of 7 to 11 treatments. It was possible to complete from 8 to 10 separate spray experiments each winter. Blue mold affects the crop in several ways, and spraying results have been measured in terms of leaf disease and plant-survival counts. The greenhouse work has been checked and supplemented by extensive tests conducted in plant beds at the Georgia Coastal Plain Experiment Station, Tifton, Ga.; the Pee Dee Experiment Station, Florence, S. C.; tobacco branch stations at McCullers and Oxford, N. C.; the Arlington Experiment Farm, Arlington, Va.; and the branch station of the Maryland Agricultural Experiment Station at Upper Marlboro, Md.

FUNGICIDAL VALUE OF VARIOUS SUBSTANCES

OILS

Tests were made with a wide variety of oils, and the data in table 1 will serve to show the great range in effectiveness of different oils. All the oils in this experiment were used at the 1-percent level excepting olive, pine, and sperm oils, which were used at the ½-percent level because at 1 percent they caused leaf injury. The oils were emulsified with Vatsol O. T. C.[3] at the rate of 1 pound per gallon.

TABLE 1.—*Fungicidal value of various oils*

Kind of oil	Diseased leaves[1]				
	Plot 1	Plot 2	Plot 3	Plot 4	Mean[2]
	Number	*Number*	*Number*	*Number*	*Number*
Beef suet	16	17	35	30	24.50
Castor	21	17	30	34	25.50
Coconut	15	30	27	19	22.75
Cod-liver	0	3	4	8	3.75*
Corn	0	3	2	9	3.50*
Cottonseed	1	10	3	13	6.75*
Eucalyptus	14	13	26	39	23.00
Linseed	0	0	3	3	1.50*
Olive	21	20	27	38	26.50
Palm	12	15	27	37	22.75
Paraffin	25	30	31	36	30.50
Peanut	3	1	12	17	8.25*
Pine	29	25	33	37	31.00
Rapeseed	1	4	5	16	6.50*
Sesame	9	1	16	7	8.25*
Soybean	0	3	0	2	1.25*
Sperm	8	12	3	3	6.50*
Tung	1	1	4	4	2.50*
Check	22	23	27	26	24.50
Check	21	20	31	39	27.75
Average					26.13

[1] Total number of leaves exposed in each plot, 45.

[2] Values significantly lower than the average of the 2 checks (8 plots) at the 1-percent level are indicated by an asterisk (*).

[3] This detergent was reported by the manufacturer to have as its active ingredient 10 percent of sodium dioctyl sulfosuccinate.

As the data in table 1 indicate, tung, linseed, soybean, rapeseed, sesame, and cottonseed oils all gave good control of blue mold. On the other hand, beef suet, castor, coconut, eucalyptus, olive, paraffin, palm, and pine oils gave no significant reduction in the amount of disease. Paraffin oil in some experiments actually increased the amount of disease injury. Other oils tested, but not included in this experiment, were chaulmoogra, cade, copaiba, cedarwood, clove, lemon, mirbane, mustard, origanum, peach-kernel, sassafras, turtle, and resin. Most of these had little or no fungicidal value. Since oils of the fungicidally active group were all of the glyceride type, it is of interest to compare their fatty acid content with the fatty acid content of the fungicidally inactive group of glyceride oils.

The data in table 2 represent average values as reported by Jamieson (*8*) and Lewkowitsch (*9*), and it may be noted first that both fungicidal

TABLE 2.—*Fatty acid content of fungicidal and nonfungicidal glyceride oils*

Group and kind of oil	Predominant fatty acid									
	Oleic	Linoleic	Linolenic	Eleostearic	Ricinoleic	Palmitic	Lauric	Chaulmoogric	Stearic	Myristic
Fungicidal:	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Cottonseed	30	45								
Corn	43	50								
Linseed	11	39	36							
Peanut	55	23								
Soybean	45	35								
Tung	13			73						
Nonfungicidal:										
Beef tallow	(1)						(1)		(1)	
Castor					80					
Coconut							44			24
Chaulmoogra								(1)		
Olive	85									
Palm	43					36				

[1] Present in appreciable amount but exact figure not available.

and nonfungicidal oils contain much oleic acid, so that fungicidal activity cannot be easily correlated with the occurrence of this fatty acid. Linoleic acid, however, occurs in large amounts in most of the fungicidal oils, but not to any extent in the nonfungicidal oils. There are strong indications also that linolenic acid (linseed oil) and eleostearic acid (tung oil) are associated with positive fungicidal activity; as is also licanic acid (oiticica oil), which is closely related to eleostearic acid. These make up a compact group of fatty acids having 18 carbon atoms and 30 to 32 hydrogen atoms. Ricinoleic, palmitic, lauric, chaulmoogric, stearic, and myristic acids were apparently not active fungicides.

COPPER AND SULFUR COMPOUNDS

Extensive tests were made on all copper compounds obtainable. The results were not of sufficient value to be given in detail. Mixtures such as bordeaux and copper-soap sprays delayed the development of the disease sufficiently to give fair control under favorable conditions. However, with severe outbreaks, when protection is most desired, they have failed. Similarly, partial but unsatisfactory control has been obtained with sulfur sprays, such as Sulfocide and Yarwood's

resin-lime sulfur, which also had the disadvantage of retarding growth. The most serious disadvantage of the use of copper or sulfur compounds alone is that a greater proportion of sprayed plants than of unsprayed plants may die after being transplanted.

COPPER-OIL SPRAYS

The comparative effectiveness against blue mold of sprays containing oil alone, copper alone, and the two in combination is indicated by the data in table 3, which give the results of a representative greenhouse experiment.

TABLE 3.—*Fungicidal value of copper and oil sprays alone and in combination*

Copper and oil sprays	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Plot 6	Mean [2]
	DISEASED LEAVES [1]						
	Number	*Number*	*Number*	*Number*	*Number*	*Number*	*Number*
Copper oxide plus cottonseed oil	0	2	2	6	3	1	2.3
Bordeaux plus cottonseed oil	5	4	3	1	1	6	3.3
Cottonseed oil alone	4	4	14	17	10	8	9.5
Copper oxide alone	31	29	22	28	18	22	25.0
Bordeaux alone	35	41	36	42	30	32	36.0
Check	168	149	147	149	157	148	153.0
	PLANTS KILLED [3 4]						
Copper oxide plus cottonseed oil	5	14	7	15	8	7	9.3
Bordeaux plus cottonseed oil	17	10	10	8	16	16	12.8
Cottonseed oil alone	15	16	21	20	21	19	18.7
Copper oxide alone	26	34	32	29	34	29	30.7
Bordeaux alone	33	34	39	36	29	37	34.7
Check	36	37	38	36	36	38	36.8

[1] There were approximately 175 leaves per plot.
[2] Significant difference between any 2 means at 5-percent level, 6.1; at 1-percent level, 8.3.
[3] There were approximately 43 plants per plot; plant data were taken 3 weeks after the leaf data.
[4] Significant difference between any 2 means at 5-percent level, 4.0; at 1-percent level, 5.5.

The sprays were applied twice weekly, beginning January 1, 1938, and by January 20 the untreated check plants were practically defoliated. Leaf counts were made at this time, and data on plants killed were taken on February 16. Ten sprays in all were applied. Considering first the data on diseased leaves, the difference between copper oxide-oil and bordeaux-oil sprays was insignificant at the 5-percent level, and on the same basis both copper-oil sprays were significantly better than oil alone. Oil alone was much superior to either copper oxide or bordeaux alone. Passing now to the end results measured in terms of plants killed, it is to be noted that neither copper oxide nor bordeaux alone appreciably reduced plant mortality, and the maximum protection was provided by the two copper-oil combinations; the oil alone was better than either copper compound, but not equal to the copper-oil combinations. It is readily possible to show by computation that the protection provided by the combination of copper and oil is significantly greater than the sum of the protection provided by each separately. The fact that the oil portion of the copper-oil spray is more important as a fungicide than the copper, in blue mold control, is emphasized because many have erroneously regarded the copper as the active ingredient. The relative fungicidal merits of oil and copper are illustrated by figure 1.

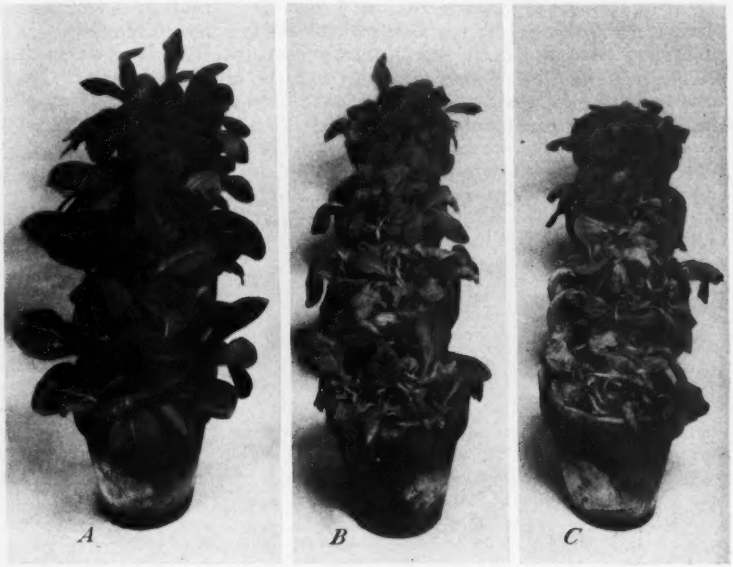

FIGURE 1.—Tobacco plants sprayed twice weekly with (*A*) 1-percent cottonseed oil and (*B*) copper oxide (Cuprocide), 1 pound per 100 gallons; *C*, untreated check. Note that the oil spray gave marked blue mold control, while the copper spray was ineffective.

The data in table 3 are from a greenhouse experiment in which disease was very severe, as indicated by the high plant mortality in the checks and the extent of disease that developed in lots receiving the best treatment. In table 4 data for a plant-bed experiment indicate that effective control can be secured with various copper compounds in addition to cuprous oxide, provided they are combined with the oil. These data also illustrate the very much higher degree of protection that can be obtained in the usual plant-bed experiment.

The results in table 4 show that all copper-oil mixtures gave effective plant-stand protection. Many leaves in the sprayed plots showed infections, but these remained small, and little or no leaf tissue was

TABLE 4.—*Fungicidal value of different copper-oil mixtures*

Spray mixture	Leaf area killed [1]				Plants killed [2]			
	Plot			Mean	Plot			Mean
	1	2	3		1	2	3	
	Percent	*Percent*	*Percent*	*Percent*	*Number*	*Number*	*Number*	*Number*
Copper tartrate plus cottonseed oil	4.70	0.55	3.43	2.89	0	0	0	0
Copper oxalate plus cottonseed oil	0	0	0	0	0	0	0	0
Copper oxide plus cottonseed oil	2.66	0	0	.89	0	0	0	0
Untreated check	93.39	93.17	97.08	94.55	30	24	35	29.

[1] Based on a 15-leaf sample taken at random in each plot.
[2] The number of plants per plot was 42 to 45.

killed. Data in table 4 are from an out-of-door plant-bed experiment, those in table 3 from a greenhouse test. As usual with the less severe plant-bed conditions, the sprays gave more perfect disease control. All readily available copper compounds have been tested in combination with oil, and particularly good results have been obtained with the oxide, resinate, oxalate, tartrate, and oxychloride. Tests with various cuprous oxides have shown slightly better results when the very finely divided yellow oxide obtained by the Raleigh (*13*) procedure was used. The ordinary commercial red and orange oxides, however, have given satisfactory results, and they are readily obtainable. In general, the results with cuprous oxide were slightly superior to those secured with other copper salts, with the possible exception of the oxalate. Earlier it was shown (table 1) that a number of vegetable oils were fungicidal, and some, e. g., tung, soybean, and corn, were slightly superior to cottonseed. Extensive tests have been conducted with these in combination with copper oxide, but none of the combinations were superior to the cupric oxide-cottonseed oil. Cottonseed oil has the further advantage of being readily available throughout the entire Southeast. However, the combination of copper oxide and soybean oil was carefully tested and proved entirely satisfactory.

As shown in table 1, certain oils used alone gave good control of mold, and such oils as tung and soybean were definitely superior to cottonseed. If copper is omitted, tobacco plants will tolerate a 2-percent oil emulsion, and careful tests were made to compare the copper-oil combination with strong oil emulsions. Results of these tests are shown in table 5.

TABLE 5.—*Fungicidal value of strong oil emulsions*

Spray	Diseased leaves [1]					
	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Mean [2]
	Number	*Number*	*Number*	*Number*	*Number*	*Number*
CuO plus 1 percent cottonseed oil	5	3	2	4	4	3.6
Oiticica oil, 2 percent	2	16	9	13	4	8.8
Tung oil, 2 percent	3	3	4	4	1	3.0
Soybean oil, 2 percent	7	13	17	15	24	15.2
Cottonseed oil, 2 percent	15	23	17	24	30	21.8
Linseed oil, 2 percent	0	0	4	4	5	2.6
Check	166	168	170	173	173	170.0
Do	175	169	168	170	173	171.0

[1] There were approximately 175 leaves per plot.
[2] Significant difference between any 2 means at 5-percent level, 3.95; at 1-percent level, 5.3.

The data in table 5 are representative of a large number of tests conducted in the greenhouse. On the whole, the best results were secured with 2-percent tung oil, and this mixture together with several others was used in a number of plant-bed experiments in 1939. In these tests, the 2-percent tung oil gave good mold control but was not quite equal to the regular mixture. Other experiments had already shown that, although under some conditions tung oil and linseed oil were superior to cottonseed oil if used alone, when combined with the copper all were equally effective. Therefore, it was concluded that, while a 2-percent oil spray could be used for blue mold control, the copper-oil combination was preferable. In general it has appeared that (1) the copper-oil combination reduced the number and size of

lesions to a minimum; (2) the oil alone greatly reduced the size of lesions but permitted a considerable number of infections; and (3) the copper alone temporarily reduced the number of infections, but this merely delayed disease development for a short time until the amount of infection had increased. These several effects are illustrated in figure 2.

FIGURE 2.—Results of spraying tobacco plants with (*A*) regular copper oxide-oil mixture (one lesion in center of third leaf from left outlined in black), (*B*) 2-percent cottonseed oil (five lesions on two leaves; small lesions indicate inactive infections), (*C*) cuprous oxide, 2 pounds per 100 gallons (seven lesions on four leaves; infections spreading rapidly). *D*, Untreated check; left to right, first three leaves completely invaded by fungus, fourth leaf severely diseased, and fifth leaf slightly so.

NUTRIENT SALTS IN COMBINATION WITH OIL SPRAYS

As will be brought out later, vegetable oils, such as cottonseed oil, at the concentrations used by the writers were not toxic to the blue mold fungus. Control of the disease apparently resulted from the development of a marked resistance by the plant that restricted the spread of the fungal hyphae after the infection had occurred. The oil penetrated the leaf tissues freely, and numerous globules could be seen in the intercellular spaces. It has seemed possible that the value of the oil sprays might be increased by the addition of nutrient salts. Thus, Henderson (*6*) found that in sand culture nitrogen and potassium both had marked influence on blue mold development. Preliminary experiments showed that 0.5 percent of sodium nitrate ($NaNO_3$) and urea, and 1.0 percent of potassium sulfate (K_2SO_4) and extract of cottonseed meal could be added to the oil sprays without injury to the plants.

Repeated experiments were made with cottonseed, tung, and linseed oils in combination with the different nutrients. In no case was the combination superior to the oil emulsion alone, and the cottonseed extract actually destroyed the fungicidal value of each oil to which it was added. As the addition of cottonseed meal extract did not cause any visible change in the mixtures, the reason for the unfavorable effect was not clear.

MISCELLANEOUS FUNGICIDES

The possibility of substituting silver nitrate for the copper oxide was investigated, and such combinations were tested both in the greenhouse and plant bed. The silver nitrate-oil mixtures had distinct fungicidal value but were not quite equal to the copper oxide-oil mixtures. Paradichlorobenzene, benzene, pentachloroethane, and xylene, all of which have value as vapor treatments, were tested in combination with oil alone, and were added to the copper oxide-oil mixture. They showed a slight value in some tests, but after careful consideration were finally discarded. Malachite green, recommended in a treatment for a similar disease of hops, showed no value against tobacco blue mold.

A number of the organic mercurials were also tested without obtaining satisfactory results.

MISCELLANEOUS ORGANIC COMPOUNDS

Early in 1939 a broad consideration of organic materials was undertaken. Each compound selected was tested with oil and also, in most cases, without oil. Alcohol, acetone, and benzene were used as solvents. A few insoluble materials were used as suspensions, with a suitable wetting and dispersing agent. Tests with each compound were continued until definite proof was obtained that it did not give adequate disease control at a phytocidal level. To date, 122 organic compounds have been tested, and all that showed fungicidal promise were included in repeated experiments.

It would be impossible to present a detailed report of these experiments, since the volume of data is necessarily large. A considerable number of the compounds tested possessed distinct fungicidal value; e. g., tetramethylthiuram disulfide, 5–hydroxyl–1, 3-dimethyl benzene, *p*-toluenesulfonyl chloride, *o*-cresyl *p*-toluenesulfonate, ferric dimethyldithiocarbamate, and salicylic acid. This last compound was first tested against blue mold at the Georgia Coastal Plain Experiment Station, Tifton, Ga., in the spring of 1939. Subsequent experiments have pointed more and more to the salicylates in general as the most promising of all the compounds studied. An indication of the comparative merits of certain salicylates and copper oxide is supplied by the data in table 6, which are from a greenhouse experiment.

The plants from which the data in table 6 were taken received 7 spray applications, the last on January 6. Conditions were ideal for the development of blue mold during the entire period of the experiment. Diseased leaves were removed as counted; hence the final column in table 6 gives the total percentage of diseased leaves. The best spray mixture was zinc salicylate, ¼ pound per 100 gallons;

TABLE 6.—*Fungicidal value of the salicylates*

Spray mixture [1] and concentration per 100 gallons	Leaves [2] diseased on—			Total
	Jan. 15	Jan. 23	Jan. 31	
	Percent	*Percent*	*Percent*	*Percent*
Zinc salicylate, ¼ pound	4.11	5.53	9.46	19.10
Zinc salicylate, ⅛ pound	7.14	13.75	20.00	40.89
Phenyl salicylate, ⅛ pound	5.53	12.32	16.96	34.81
Phenyl salicylate, 1/16 pound	10.71	16.25	19.40	46.42
Salicylamide, ¼ pound	10.19	15.17	17.86	43.22
Salicylamide, ⅛ pound	11.79	15.00	15.89	42.68
Salicylic acid, ⅛ pound	7.50	15.00	17.50	40.00
Cuprocide 54 Y 1½ pound	14.28	19.28	21.78	55.34
Untreated check	100.00	100.00	100.00	100.00

[1] Each with 1 percent cottonseed oil.
[2] There were 140 leaves per plot. Each value is the mean of 4 plots.

the plants receiving this treatment showed noticeably less disease throughout the experiment (fig. 3). Salicylamide, which is said to be the active ingredient of Shirlan A. G., used as a spray against tomato mold in England, was not equal to zinc salicylate. Among the various salicylates tested, excellent results were obtained with methyl salicylate under cool conditions; at higher temperatures, however, this material was not effective. On the other hand, benzyl salicylate, which is also a liquid, was highly effective under a wide variety of conditions. It might appear that methyl salicylate was more easily lost by vaporization, but the boiling point of methyl salicylate is 220°–224° C. and that of benzyl salicylate 208°, so this explanation would seem unsatisfactory.

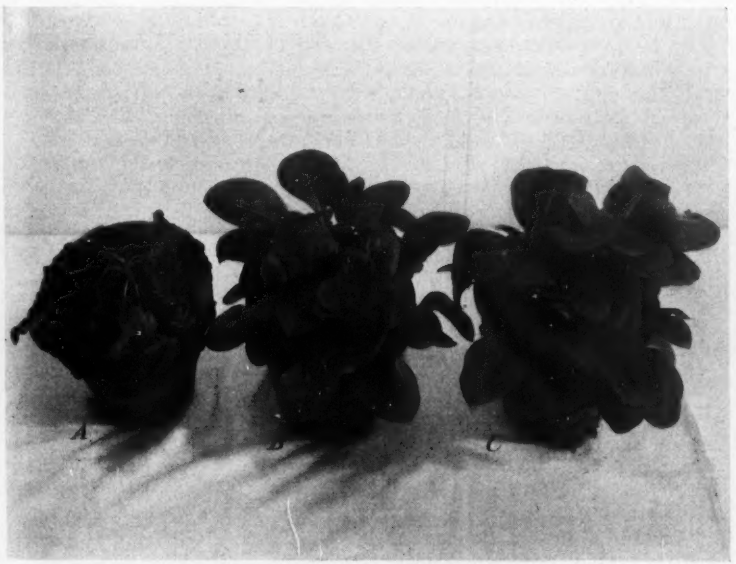

FIGURE 3.—*A*, untreated check; *B*, control of blue mold with copper oxide-oil mixture; *C*, control of blue mold with zinc salicylate-oil mixture.

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The spring of 1941 was not favorable for the development of blue mold, and the results obtained in plant-bed experiments were not decisive. Nevertheless, salicylates gave promising results. At Florence, S. C., and later at Arlington, Va., bismuth salicylate without oil showed up exceptionally well. The results of an experiment in which some of the better salicylates were used are given in table 7.

TABLE 7.—*Blue mold control in the plant bed with the salicylates*

Spray and concentration per 100 gallons	Diseased leaves							
	5 days after final spray				20 days after final spray			
	Plot 1	Plot 2	Plot 3	Mean [1]	Plot 1	Plot 2	Plot 3	Mean [2]
	No.	*No.*	*No.*	*No.*	*No.*	*No.*	*No.*	*No.*
Regular copper oxide-oil	7	4	3	4.67	28	28	32	29.33
Benzyl salicylate, ¼ pound, plus 1 gallon of oil	0	0	0	0	5	5	9	6.33
Zinc salicylate, ¼ pound, plus 1 gallon of oil	4	2	0	2.0	9	12	8	9.67
Salicylic acid, ½ pound, plus 1 gallon of oil	12	8	6	8.67	9	11	16	12.00
Bismuth salicylate,[3] 1½ pound, no oil	3	1	2	2.0	4	3	7	4.67
Untreated check	42	55	40	45.67	3	5	5	4.33

[1] Significant difference between any 2 means at 5-percent level, 6.66; at 1-percent level, 9.47.
[2] Significant difference between any 2 means at 5-percent level, 3.45; at 1-percent level, 4.91.
[3] There are two bismuth salicylates; the one used in this experiment was the basic bismuth salicylate, 64 percent Bi_2O_3.

The data in table 7 show that benzyl salicylate at a dilution of 1 to 3,200 (¼ pound per 100 gallons) plus a 1-percent oil gave perfect disease control at the time of the first disease count, which was made 5 days after the final spray application. However, all the mixtures used had given good control at the time. The last disease count was made 20 days after spraying ceased, and by this time the unsprayed check had recovered and so showed very little active disease. At this time the copper-sprayed plots were noticeably the most severely diseased and showed a marked increase of infection. Certain salicylate-sprayed plots, on the other hand, were still quite free of blue mold. This tendency of the salicylates to provide spray protection over a much longer period than the copper compounds has been observed many times.

EMULSIFIERS FOR COPPER-OIL AND SALICYLATE-OIL MIXTURES

While the vegetable oils do not emulsify as easily as mineral oils, stable preparations can readily be prepared with a wide variety of emulsifiers. The addition of copper or zinc compounds, however, greatly reduces the number of adequate emulsifiers, and still further restriction is imposed by the requirement that emulsification must be possible with waters of varying hardness. Thus, tests throughout the Southeast have shown that waters of the Coastal Plain area are quite soft, having less than 100 p. p. m. of hardness, whereas in the Piedmont belt some well waters test up to 250 p. p. m. of calcium carbonate ($CaCO_3$).

Various common soaps were tested as emulsifiers and found unsatisfactory. This was true also of sulfated vegetable oils, calcium caseinate, bentonite, kaolin, sulfite lye, gelatin, triethanolamine oleate, monoamylamine oleate, diglycol laurate, glycerol mono-

stearate, diglycol stearate, ammonium stearate, ammonium linoleate, aminostearin, and glycerol monoricinoleate. More promising results were obtained with certain members of a group of complex new synthetic detergents that have been developed recently for use particularly in the textile trade.

The development of the salicylate-oil sprays required a resurvey of the emulsifier situation. Vatsol O. T. C., which was excellent with the copper-oil mixture, could not be used in the salicylate-oil combinations. On the other hand, B1956 [4] proved very satisfactory with zinc and benzyl salicylates. An additional and reasonably priced emulsifier that was compatible with the benzyl salicylate-oil mixture, but not with zinc, was Twitchell Base 400H.[5] It was easily possible with the salicylates to make all-in-one mixtures that merely required dilution. Zinc salicylate dissolves in alcohol, acetone, or benzene, and these solutions in turn are readily soluble in oil. Benzyl salicylate, of course, is directly oil-soluble, and the B1956 emulsifier was oil-miscible. With these in an all-in-one mixture, the procedure to prepare a batch of spray was very simple. First, the proper amount of stock was measured out, a little water was added, and the mixture was then forced through a spray nozzle, which produced effective emulsification. The emulsion was then diluted to the proper volume.

TOXICITY OF OILS, CUPROUS OXIDE, AND BISMUTH SALICYLATE TO SPORES OF PERONOSPORA TABACINA

McCallan and Wilcoxon (*11*), Horsfall et al. (*7*), and other workers have found the spore-germination test a valuable aid in their efforts to develop an adequate laboratory method for the evaluation of copper fungicides. It is obvious that if other spray materials could be quickly tested in the laboratory and even approximate results obtained, much laborious greenhouse and field work would be saved. The writers made germination tests with cottonseed oil, palm oil, and cuprous oxide. Spores on a slide treated with 1-percent oil, or in actual drops of the oil emulsions, germinated normally. Although cottonseed oil controls blue mold and palm oil does not (table 1), the germination of *Peronospora tabacina* spores was higher with cottonseed than with palm oil emulsion or with tap water. Cuprous oxide, at the concentration used for spraying, inhibited all spore germination. Thus, the spore-germination tests would lead to the conclusion that cuprous oxide is a very effective spray and that cottonseed oil is completely ineffective. Figure 1 and table 3 show that this is not the case and consequently that the fungicidal value of the oils cannot be explained on the usual basis of protective leaf coatings that destroy the disease-producing spores before penetration and infection can occur.

Spore-germination experiments were also conducted to measure the comparative toxicity of cuprous oxide and bismuth salicylate. The former (table 3) was ineffective as a blue mold spray unless combined with oil, while the latter (table 7) used alone gave good control. In conducting the spore toxicity tests the initial concentration of each material was the same as had previously been used in the sprays, and a sufficient series of dilutions was made to cover the entire range

[4] A phthalic anhydride glycerol alkyl resin.
[5] Reported by the manufacturer to be a sulfonated mineral oil.

from complete inhibition of spore germination to complete absence of measurable toxicity. The lowest concentration of cuprous oxide definitely toxic to the spores was 0.0058 pound per 100 gallons; that of bismuth salicylate, 0.094 pound per 100 gallons. On this basis, the copper compound was about 16 times the more toxic. The lowest concentration of cuprous oxide that completely inhibited all spore germination was 0.094 pound per 100 gallons; that of bismuth salicylate, 0.375 pound per 100 gallons. On this basis, the copper compound was 4 times the more toxic.

There were other interesting differences between these two materials. Under the microscope the cuprous oxide particles appear as irregular solid masses. The bismuth salicylate particles are also very small and, furthermore, each particle is a group of slender crystals that tend gradually to separate. With the aid of Vatsol O. T. C., the bismuth makes an excellent suspension. The effect of cuprous oxide and bismuth salicylate on the fungus spores also is different. Cuprous oxide in toxic amounts causes marked cell plasmolysis, whereas bismuth salicylate, even in concentrations that inhibit germination, produces no plasmolysis.

DISCUSSION

For many years, copper fungicides have been relied upon almost exclusively for the control of fungus diseases of the herbaceous crops. The present war situation has made it quite apparent that fungicides requiring little or no copper would be most desirable. Therefore, the results of the study reported here, which deal entirely with the control of the blue mold disease of tobacco, may have a broader significance. Furthermore, it is of interest to note that the vegetable oils, and particularly such materials as bismuth and benzyl salicylate, offer promise not merely as substitutes for copper but as materials that may actually be superior to copper compounds in convenience and in disease control.

Again, the usually accepted explanation of spray protection against diseases is that, by coating the exposed leaf or fruit surface with a fungicide, the germinating spores are destroyed and infection is prevented. Anyone familiar with plant-bed culture of tobacco can appreciate that in the latter stages of growth, when the plants form a solid mass of foliage with many leaves close to the ground, it would be impossible to coat all leaf surfaces with a fungicide. In the spraying work here reported this has not been attempted, the effort being (1) to coat exposed surfaces and (2) to apply the spray three or four times before the disease developed. It has been shown that the oils differ greatly in fungicidal value against blue mold and that these differences have been associated with the glyceride content. Oils containing appreciable amounts of linoleic, eleostearic, or licanic glycerides had strong fungicidal value, while oils containing lauric, myristic, palmitic, chaulmoogric, oleic, and stearic glycerides were inactive. Indicating different reactions with different diseases, Fajans and Martin (*4*) reported that cuprous oxide plus mineral oil was superior to cuprous oxide plus cottonseed oil against late blight (*Phytophthora infestans* (Mont.) D By.) of potato. This is the direct reverse of the results the writers have obtained with blue mold.

It is of interest to consider just how such a material as cottonseed oil functions in blue mold control. The oil acts as a sticker for the

copper, but ineffective oils are just as good stickers. The oil-sprayed leaves dry earlier in the morning, and also sooner after rains, than the leaves of unsprayed plants, but here again ineffective oils also favor quick drying of leaves. Finally, spores of the blue mold fungus germinate as readily in 1-percent cottonseed oil as in clear water. The oil-sprayed leaves become a darker green after three or four applications (fig. 4), and microscopic examination of the tissues at this stage shows numerous oil globules in the intercellular spaces. When such leaves become infected, the mycelium spreads for a short time, then ceases to grow. Ultimately only a small area is killed, instead of an entire leaf. The visible reaction of the invaded oil-treated tissues is the same as the reaction of leaf tissue possessing genetic resistance (such as the *Nicotiana tabacum* × *N. debneyi* tetraploid). Thus, it appears that the oil-treated leaves are resistant to blue mold, and that in some manner certain oils promote the development of this resistance.

Since the presence of the oil inside the leaf has the effect just described, it might be thought that similar resistance could be built up with copper, but this does not appear to be the case. Thus, De Ong (*3*) has shown that, with a copper compound dissolved in an oil, considerable amounts of the copper could be recovered from the leaf tissues, whereas the usual copper spray remained on the surface, except for traces. However, De Ong's mixture of copper resinate in pine oil was no more effective than bordeaux against blue mold. The writers recognize that blue mold in many respects behaves very differently from other downy mildews of vegetable crops. Probably the usual type of copper spray mixture, such as bordeaux, and applications designed to coat all exposed plant surfaces with a protective layer are generally the most practical. Certainly, however, this type of spray mixture was not effective against blue mold. The writers' findings suggest that concentration of spray investigations on materials known to be highly toxic to fungus spores may lead to valuable chemotherapeutic agents being overlooked. This is further supported by recent developments in the field of medical pathology. Thus, Long and Bliss (*10*) stated, with regard to such materials as sulfanilamide and sulfapyridine, that no simple explanation has been evolved as to their mode of action. Again, Findlay (*5*) concluded that there is no reason to suppose that chaulmoogra oil acts directly on the causal organism of leprosy, and there is evidence that the condition of the patient has a bearing on the success of the treatment. This latter observation fits in with observations on oil protection against blue mold. Thus, tobacco plants growing in the open, exposed to bright sun, are almost perfectly protected against blue mold by the copper-oil spray; on the other hand, plants that are shaded or grown in the greenhouse in midwinter are much less effectively protected by the spray treatment.

Search for spray mixtures superior to the copper oxide-cottonseed oil combination has recently been centered on the salicylates. A number of these compounds gave marked blue mold control, but the best results have been obtained with benzyl salicylate used with 1 percent oil, and bismuth salicylate without oil. The salicylate sprays have shown superior disease control, and a notable feature has been the prolonged nature of the protection. Bismuth salicylate, which gave excellent blue mold control when used alone, in contrast

FIGURE 4.—Plants in (*A*) unsprayed plot and (*B*) plot sprayed with copper-oil mixture, about 2 hours after a rain. The oil-sprayed plants dried more quickly than the unsprayed plants, and the sprayed leaves were a much darker green.

to cuprous oxide, which is ineffective without the oil, was only ¼ to 1/16 as toxic to the spores of *Peronospora tabacina* as cuprous oxide. Thus it was again indicated that fungicidal value could not be measured in terms of ability to inhibit spore germination.

SUMMARY

Emulsified oils used as sprays differed greatly in their effectiveness against the blue mold disease of tobacco.

Soybean, linseed, cottonseed, tung, oiticica, and peanut oils were strongly fungicidal. Olive, castor, palm, coconut, chaulmoogra, beef tallow, pine, and paraffin oils were nonfungicidal.

Fungicidal properties appeared to be associated with the presence of linoleic, linolenic, eleostearic, and licanic glycerides.

The tobacco leaves sprayed with a fungicidal oil showed numerous oil globules in the intercellular spaces, and such leaves were resistant to fungal invasion.

A mixture of cottonseed or other fungicidal oil with a copper compound gave more effective blue mold control than the oil alone. Copper oxide alone was almost completely ineffective.

The only emulsifiers that proved satisfactory with copper and oil mixtures were a few of the complex sulfonated alcohol type.

In a search for fungicides that could be used in place of either or both copper and oil, 122 organic compounds were tested.

The salicylates showed strong fungicidal value against blue mold; the most effective were benzyl salicylate with oil, and bismuth salicylate without oil.

Spore-germination tests showed (1) that cuprous oxide inhibited the germination of spores at ⅛ spray strength, (2) that bismuth salicylate was only ¼ to 1/16 as toxic as cuprous oxide, and (3) that cottonseed oil was nontoxic at full spray strength. The spore-germination tests consequently gave no indication of the disease-control value of the several sprays as shown by previous experiments.

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FUNGICIDAL AND PHYTOCIDAL PROPERTIES OF SOME METAL DIALKYL DITHIOCARBAMATES [1]

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INTRODUCTION

The insecticidal value of some metal dialkyl dithiocarbamates has been determined by Guy (*5*),[2] but little information on their fungicidal and phytocidal properties has been published. As early as 1929 Hand (*6*) patented the manufacture and the insecticidal uses of compounds formed by the union of carbon disulfide and organic bases or amines to form the grouping —C—, and in 1934 Tisdale and
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Williams (*10*) patented the use of the derivatives of dithiocarbamic acids as disinfectants. In 1927 Cadwell (*1*) patented the use of normal butyl thiocarbonic acid disulfide as a deodorant and in 1929 (*2*) the process of making the substituted dithiocarbamates. In none of the above references were there reports of experiments on the effectiveness of the dithiocarbamic acid derivatives against fungi growing on plants.

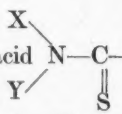
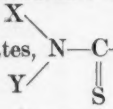
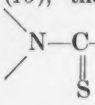
Moore, Montgomery, and Shaw (*9*), Montgomery and Moore (*8*), and Marsh (*7*) reported experiments in which derivatives of dithiocarbamic acid were used as fungicides on plants. All these investigators used the thiuram disulfides, and Marsh used zinc diethyl dithiocarbamate in addition. The thiuram disulfides were better fungicides than zinc diethyl dithiocarbamate and were not injurious to apple. In this paper are reported the results of experiments to determine the fungicidal properties of various metal salts of some dialkyl dithiocarbamates and their effects when sprayed on plants.

MATERIALS AND METHODS

Some of the dithiocarbamates, which are commonly used in the vulcanization of rubber, were supplied by the R. T. Vanderbilt Co., of New York, N. Y., and E. I. du Pont de Nemours & Co., Inc., of Wilmington, Del.; others were made in the laboratories of the United States Horticultural Station, Beltsville, Md. For the field tests described in this paper the iron and lead dimethyl dithiocarbamates were furnished by E. I. du Pont de Nemours & Co., and the R. T. Vanderbilt Co., respectively.

The substituted dithiocarbamates are made by treatment of the substituted primary and secondary aliphatic and aromatic amines with carbon disulfide in alkaline alcoholic solutions. As an example,

[1] Received for publication June 9, 1942.
[2] Italic numbers in parentheses, refer to Literature Cited, p. 291.

dimethyl amine in alcoholic solution, when treated with carbon disulfide and sodium carbonate, yields sodium dimethyl dithiocarbamate. One mole of an amine combines with one mole of carbon disulfide to form the dithiocarbamic acid  . X and Y may represent hydrogen or an alkyl radical. The hydrogen attached to sulfur dissociates and may be replaced by sodium to form a soluble dithiocarbamate or by the heavy metals to form insoluble dithiocarbamates,  . Z may be a metal or any salt-forming organic or inorganic radical. A considerable range of physical properties is made available by changing the substituents at X, Y, and Z. According to Hand (*6*) and Tisdale and Williams (*10*), the essential pesticide grouping of these compounds is  .

PHYSICAL PROPERTIES OF TESTED METAL DIALKYL DITHIOCARBAMATES

Some of the physical properties of the various metal dialkyl dithiocarbamates are shown in table 1. Those obtained from the rubber-chemical industry did not differ materially from their counterparts prepared by the writers. Aqueous solutions of the soluble sodium salts, as received, exhibited an alkaline reaction, while derivatives of the heavy metals were acid or neutral. For the most part, the heavy metal salts were very slightly soluble in distilled water. The dimethyl salts were usually more soluble than those of the diethyl and dibutyl series, and the iron and zinc salts of the dimethyl series were considerably more soluble than the others of that group. Most of the metal dialkyl dithiocarbamates were easily suspended in either distilled or tap water. None of the compounds made up in the writers' laboratories possessed any particular odor. The commercial sodium compounds used by the writers as reagents for the formation of metal derivatives [3] possessed a strong disagreeable odor. Since the dimethyl and diethyl metal dithiocarbamates obtained from the chemical companies also possessed this same odor, it is suggested that they had not been freed of the sodium reagent used in their preparation. On standing in contact with air, the iron dimethyl dithiocarbamate prepared by the writers generated an odor resembling that of carbon disulfide. The butyl derivatives of lead and silver were difficult to make, and their physical properties indicated the presence of impurities. Because of this the data obtained with the silver and lead salts, although included in the tables, are not considered fully reliable.

[3] For suggesting the preparation of the heavy metal salts by mixing solutions of sodium salts with solutions of inorganic salts of heavy metals, the writers are indebted to Paul I. Murrill, formerly chief chemist of the R. T. Vanderbilt Co.

TABLE 1.—*Chemical and physical properties of the metal dialkyl dithiocarbamates tested*

Substituted dithiocarbamate	Source [1]	Physical nature	Melting point (uncorrected)	Appearance	Wettability in water	Solubility in distilled water of room temperature	pH (glass vs. saturated calomel electrode)
			°C.			*P. p. m.*	
Sodium dimethyl	Vanderbilt; Du Pont	Liquid (solid in solution).		Colorless	Complete	>1,000	10.5
Sodium diethyl	Vanderbilt	Solid	85 to 95	White	do	>1,000	10.0
Sodium dibutyl	Vanderbilt; Du Pont	Liquid (solid in solution).		Reddish orange	do	>1,000	9.9
Iron dimethyl	Beltsville; Du Pont	Solid	Dec.[2]	Very dark brown	do	120	5.0
Iron diethyl	Beltsville	do	251	Dark chocolate brown	Difficult	40	5.9
Iron dibutyl	do	do	245	Black; a gray precipitate appeared during preparation, but disappeared later.	Complete	12	7.4
Zinc dimethyl	Beltsville; Vanderbilt	do	246	White	do	65	6.5
Zinc diethyl	Beltsville	do	175	do	Difficult	13	5.6
Zinc dibutyl	Beltsville; Vanderbilt	do	104.5	do	do	52	7.0
Lead dimethyl	do	do	Dec. 305	do	Complete	44	6.4
Lead diethyl	Beltsville	do	204	do	do	22	5.9
Lead dibutyl	do	do	77	Orange yellow turning gray brown on standing; dry pure substance white.	do	18	6.0
Copper dimethyl	Beltsville; Vanderbilt	do	Dec. 305	Brown	do	12	4.3
Copper diethyl	Beltsville	do	201	Chocolate brown	do	12	5.6
Copper dibutyl	do	do	77 [3]	A black hard crystalline substance; suspension that would not settle was discarded.	do	18	4.3
Silver dimethyl	do	do	Dec. 289	Grayish white	do	8	5.3
Silver diethyl	do	do	175	do	do	11	5.5
Silver dibutyl	do	do	107	White; a red and an orange contaminant appearing during preparation removed by recrystallization.	do	18	5.5
Mercury dimethyl	do	do	214	Faintly yellowish white	do	20	5.5
Mercury diethyl	do	do	112	Very light yellow	do	12	5.7
Mercury dibutyl	do	do	101	Dirty white	do	11	5.3
Selenium diethyl	Vanderbilt	do	67	Yellowish white turning drab to brown on handling.	Difficult		6.8

[1] Vanderbilt = R. T. Vanderbilt Co.; Du Pont = E. I. du Pont de Nemours & Co, Inc.; and Beltsville = fungicide laboratory, U. S. Horticultural Station, Beltsville, Md.
[2] Decomposes before melting.
[3] Not sharp; evidence of contamination.

It cannot be taken for granted that carefully weighed equivalents of a soluble dialkyl dithiocarbamate and of a soluble salt of a heavy metal will unite only by replacement of the hydrogen attached to sulfur. In the first place, as shown in table 1, the soluble salts of these compounds display an alkaline reaction when dissolved in water. Furthermore, if one of these solutions is neutralized or acidified the free acid appears as a precipitate. Most of the solutions of salts of heavy metals that would be used to prepare the heavy metal dialkyl dithiocarbamates are neutral if not acid, and basic salts are precipitated if these solutions are neutralized or made alkaline. Accordingly the solutions intended for the preparation of a desired heavy metal dialkyl dithiocarbamate must be made up as nearly neutral as possible and must be mixed with all customary precautions to avoid inclusions, entrainment, and local exhaustion of reactants. Even with the best of care some contamination with basic salts of the heavy metals and dialkyl dithiocarbamic acid is to be expected. In the laboratory the solution of the sodium salt was run into the solution of the heavy metal salt slowly and with thorough stirring. Extraction with an organic solvent would then remove the basic salts.

In the second place the dialkyl dithiocarbamates oxidize very readily. The most usual course is the elimination of the dissociable hydrogen from each of two molecules, which then combine to form a tetraalkyl thiuram disulfide. This product is insoluble and appears not to combine with metals. This propensity makes difficult the preparation of heavy metal salts in their highest state of oxidation, for example, ferric dialkyl dithiocarbamates.

Examinations of the iron salts used in this study have raised doubts regarding their composition. On storage also these materials gave evidence of changes. Conflicting reports from workers who have tested these substances in the field have given the impression that their supplies were not alike. It is suggested that even though a solution of ferrous sulfate is used in the preparation, oxidation of the organic residue takes place to some extent. Attempts to separate by extraction a substance with the theoretical iron content will not be reported here. Supplies of iron dialkyl dithiocarbamates used by others for insecticidal and fungicidal tests are probably similar in composition to those studied by the writers.

EXPERIMENTAL PROCEDURES AND CONDITIONS

The phytocidal properties of the various compounds were determined by spraying Red Kidney bean (*Phaseolus vulgaris* L.) and various varieties of peach (*Amygdalus persica* L.) and of apple (*Malus pumila* Mill.), all in vigorous condition. (See table 2.) The dialkyl dithiocarbamates, when applied to apple, were combined with lime and lead arsenate at the rate of 2 pounds of the metal dialkyl dithiocarbamate, 8 pounds of hydrated lime, and 2 pounds of acid lead arsenate to 100 gallons of spray fluid. The lead arsenate was added for the control of insect pests and the lime as a "safener" against arsenical injury, since it was not known whether the dialkyl dithiocarbamates possessed insecticidal properties. On bean and peach, the dialkyl dithiocarbamates were used with lime but without lead arsenate. The sprays were applied to bean and small limbs of peach and apple with a hand sprayer several times during the season. Only

in the amount of pressure used did these small-scale experiments differ from the more extensive tests reported on page 287.

The fungicidal properties were determined according to the methods outlined by Goldsworthy and Green (*3*, *4*). *Sclerotinia fructicola* (Wint.) Rehm (the peach brown rot pathogen) and *Glomerella cingulata* (Ston.) Spauld. and Von Schrenk (the apple bitter rot pathogen) grown under standardized environmental conditions were used as the test organisms. The tests included subjecting conidia to saturated distilled-water solutions of the materials during a 24-hour perfusion period, and to residues from the chemicals, with and without adjuvants, sprayed on glass cover slips and allowed to weather.

The perfusion tests (*4*) were conducted with solutions obtained by saturating 2 liters of distilled water with an excess of the chemical. Not less than 7 days was allowed for the solid and solvent to reach equilibrium. The equilibrium solution thus obtained was then passed through a special perfusion apparatus so that it came in contact with conidia in sterile water-agar cubes. During the 24-hour perfusion period, tests of the fungicidal activity of these solutions were usually made at the end of 2, 4, 6, 22, and 24 hours. Each test was made by removing one of the conidia-containing agar cubes from the perfusion cells, examining one half of it under the microscope for conidial germination, and placing the other half on sterile oxidized potato-juice 4-percent agar to test growth capability. Observations on germination were recorded at the time the cubes were taken out of the equilibrium solution and after a 24-hour incubation period on the potato agar. (See table 4.)

In 1941 spray-residue tests (see table 2) were conducted in the following manner. The chemicals used were mixed at the rate of 2 pounds of the test material, 8 pounds of hydrated lime, and 2 pounds of lead arsenate to 100 gallons of spray fluid, and the mixture was sprayed on thin glass cover slips. The spraying of the agitated mixture on the glass cover slips was done at a standard pressure and for a given time, and the resulting residues represent similar loads, at least for any given mixture. For each chemical 12 cover slips were prepared as indicated. These were then suspended in unsprayed apple trees by means of special holders so that rain, dew, wind, temperature changes, leaf excretions, insects, fungi, light, carbon dioxide concentration, and other factors could operate and perhaps change their physical and chemical properties from day to day. Some of the glass cover slips were brought into the laboratory every other day to test the fungicidal properties of the residues. This was done by determining their degree of toxicity to the conidia of *Sclerotinia fructicola* and *Glomerella cingulata* by a standardized procedure (*3*). Since the testing period usually lasted about 2 weeks (a length of time often elapsing between applications of orchard sprays), seven separate tests of a residue were made during that time. All these tests were made during the regular spraying season, and the results are somewhat indicative of what the materials will do under orchard conditions.

Rainfall and temperature are not recorded in table 2, since space does not permit the inclusion of the continuous records obtained during the tests. The experiments summarized in table 2 were conducted during three separate 2-week periods. During these periods temperatures were mostly moderate, and 1.5, 3.4, and 1.84 inches of

rainfall were recorded for the respective periods. In all of these tests the residues were subjected to precipitation and other weather conditions sufficient to provide a rigid test of their sticking and weathering properties.

The fungicidal and phytocidal properties of combinations obtained by tank mixing of sodium dimethyl dithiocarbamate with ferrous sulfate, zinc sulfate, and lead acetate, respectively, to form ferric, zinc, and lead dimethyl dithiocarbamates were tested. (See table 3.) The combinations were used alone and in some cases with lead arsenate, lime, lead arsenate and lime, bentonite, bentonite and lime, or bentonite and nicotine sulfate, which have been used in combination for control of the codling moth.[4] These tests were made during three 2-week periods in which 1.84, 1.55, and 2.18 inches of rainfall, respectively, were recorded. Temperatures were mostly moderate.

During the 1941 season field tests were conducted on apple, peach, and cherry at the United States Horticultural Station, Beltsville, Md., and on apple at Mountain Grove, Mo., with a commercial sample of ferric dimethyl dithiocarbamate. Lead dimethyl dithiocarbamates, consisting of a sample of the pure material and of one in which the lead compound was diluted 70 percent with china clay, were also tested on apple at the Maryland station.

The season was unfavorable for the production of apple scab, caused by *Venturia inaequalis* (Cke.) Wint., at the Maryland station, but favorable for the disease at the Missouri station. At the Maryland station cherry leaf spot, caused by *Coccomyces hiemalis* Hig., was plentiful; and the season was favorable for peach scab, caused by *Cladosporium carpophilum* Thüm., but not for brown rot, caused by *Sclerotina fructicola*. In Maryland the growing season was marked by an absence of rainfall at the beginning and end and by an abundance of rainfall during the remainder. The temperatures, as a whole, were moderate, sometimes rather cool but seldom hot (fig. 1). The season was favorable for the production of copper and arsenical injury, but not for sulfur injury. The effect of drought was extreme by the end of the growing season. In Missouri the early and middle parts of the growing season were marked by a general abundance of rainfall accompanied by moderate temperatures. Rainfall was 7.67 inches in April, 4.07 in May, 2.86 in June, 6.17 in July, 1.01 in August, and more than 10 in September.

EXPERIMENTAL RESULTS

PERFUSION AND SPRAY-RESIDUE TESTS

The phytocidal data presented in table 2 show that the lead dialkyl dithiocarbamates tested were safely applied to all the plants used. Of the iron compounds tested, the dimethyl compound caused injury to peach. This injury developed after a period of weathering, indicating that this material was unstable. None of the zinc compounds tested was injurious to apple, but the dimethyl and diethyl compounds caused delayed injury to bean foliage; on peach the diethyl compound of zinc caused injury of the same type as the ethyl compound of iron but of a lesser degree. All of the copper, selenium, and mercury compounds used proved to be injurious to the test plants,

[4] STEINER, L. F., SAZAMA, R. F., FAHEY, J. E., and RUSH, H. W. TANK-MIX NICOTINE-BENTONITE FOR CONTROL OF THE CODLING MOTH. U. S. Bur. Ent. and Plant Quar. Cir. E-428. [Processed.]

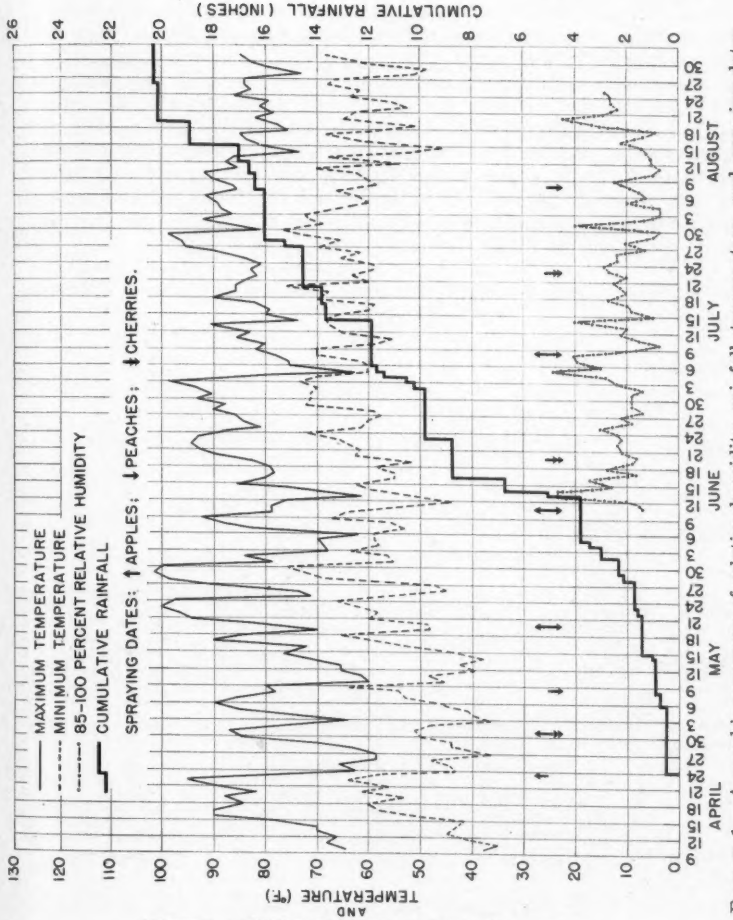


FIGURE 1.—A graphic summary of relative humidity, rainfall, temperature, and spraying dates at the United States Horticultural Station, Beltsville, Md.

and the silver dibutyl compound was injurious to bean and peach. The mercury compounds proved to be the most injurious of those tested. The injury caused by the iron and zinc compounds may properly be described as a leaf-spotting or shot-hole effect. Very little marginal leaf injury and no bark or fruit symptoms were noted. The injury caused by the silver, selenium, copper, and mercury compounds, on the other hand, was of a more pronounced character. The leaves of peach and bean and the bark of young peach twigs were severely injured; not only leaves spotted, but marginal injury, yellowing, and leaf fall were common. On apple, spot necrosis, marginal necrosis, and yellowing of leaves were common, but bark injury and leaf fall did not occur. On peach fruits necrosis was observed where moisture accumulated, and on apple fruits a superficial russeting developed. None of the metal dialkyl dithiocarbamates prevented the typical arsenical injury from developing on the leaves and bark of peach when lead arsenate was present in the mixture. The zinc compounds appeared to cause the least of this type of injury.

TABLE 2.—*Small-scale tests of phytocidal and fungicidal properties of some metal dialkyl dithiocarbamates*

Substituted dithiocarbamates [1]		Injury caused by spray residue to—			Duration [3] of toxicity of spray residues [2] to—	
Metal	Alkyl group	Bean	Apple [2]	Peach	*Sclerotinia fructicola*	*Glomerella cingulata*
					Days	*Days*
Sodium	Dimethyl	Severe				
	Dimethyl (with lime)		None	None	13	13
	Diethyl					
	Diethyl (with lime)		None	None	0	0
	Dibutyl	Moderate		Moderate		
	Dibutyl (with lime)		None	None	0	0
Ferric	Dimethyl	None	do	Slight	13	13
	Diethyl	do	do	None	0	0
	Dibutyl	do	do	do	0	0
Zinc	Dimethyl	Moderate	do	do	13	13
	Diethyl	do	do	Moderate	4	4
	Dibutyl	None	do	None	0	0
Lead	Dimethyl	do	do	do	13	13
	Diethyl	do	do	do	6	6
	Dibutyl	do	do	do	0	0
Copper	Dimethyl	Moderate	Moderate	Moderate	13	13
	Diethyl	do	do	do	6	6
	Dibutyl	do	do	do	0	0
Silver	Dimethyl	None	None	None	13	13
	Diethyl	do	do	do	13	13
	Dibutyl	Moderate	do	Moderate	0	0
Mercury	Dimethyl	do	Moderate	do	13	13
	Diethyl	do	do	do	13	13
	Dibutyl	do	do	do	13	13
Selenium	Diethyl	do	do	do	13	13

[1] In all these experiments heavy metal dialkyl dithiocarbamates were used at the rate of 2 pounds with 8 pounds of lime per 100 gallons of spray fluid. The sodium salt with or without lime was used at the same strength.

[2] Lead arsenate at the rate of 2 pounds to 100 gallons of spray fluid was added for insect control on apples and in tests of toxicity of spray residue to conidia.

[3] Testing period lasted 2 weeks.

In the experiments presented in table 3, where the metal dimethyl dithiocarbamates were made up in the spray tank by mixing stoichiometrical equivalents of the reacting soluble salts, no injury resulted from the use of the lead combinations, but the zinc and iron salts caused injuries similar to those listed in table 2. When the tank-mixed

iron salt was combined with bentonite only, no injury developed even on peach. When the sodium dimethyl dithiocarbamate was used in excess injury developed on peach, but if the iron sulfate was in excess no injury developed (table 3). Combinations of tank-mixed iron dimethyl dithiocarbamate, nicotine sulfate, and bentonite, on the other hand, caused injuries on peach similar to the mixture containing lime.

These data indicate that the iron, zinc, and lead salts may be safely applied to apple and that the lead salts may be safely applied to peach. None of the others appear promising.

TABLE 3.—*Small-scale orchard tests of fungicidal and phytocidal properties of iron, zinc, and lead dimethyl dithiocarbamate spray combinations with various adjuvants*

Combination (No. and description)	Rainfall during test	Injury caused by spray residue to—		Duration of toxicity of residues to—	
		Apple	Peach	*Sclerotinia fructicola*	*Glomerella cingulata*
	Inches			*Days*	*Days*
1. Tank-mix iron salt [1]	1.84	None	Slight	12	12
2. No. 1 + lead arsenate (2 lb.)	1.84	do	do	12	12
3. No. 1+lead arsenate (2 lb.)+hydrated lime (8 lb.)	1.84	do	do	12	12
4. No. 1+hydrated lime (8 lb.)+bentonite (2 lb.)	1.84	do	do	4	4
5. No. 1+bentonite (4 lb.)+nicotine sulfate (1 pt.) added in order given (A, B, C, and D).[2]	2.18	do	do	13	13
6. Same as No. 5 but materials added in the order B, A, C, and D.[2]	2.18	do	do	13	13
7. Same as No. 5 but materials added in the order C, A, B, and D.[2]	2.18	do	do	13	13
8. Same as No. 5 but materials added in the order C, B, A, and D.[2]	2.18	do	Considerable.	13	13
9. No. 1 (half strength)+bentonite (5 lb.)	2.18	do	None	13	13
10. No. 9+excess sodium dimethyl dithiocarbamate (0.5 lb.).	2.18	do	Slight	13	13
11. No. 9+excess ferrous sulfate (0.5 lb.)	2.18	do	None	13	13
12. Tank-mix zinc salt [3]	1.55	do	Slight	13	13
13. Tank-mix lead salt [4]	1.55	do	None	13	13
14. No. 13+hydrated lime (4 lb.)	1.55	do	do	13	13
15. No. 13+hydrated lime (4 lb.)+lead arsenate (2 lb.)	1.55	do	Slight	13	13
16. Clay lead salt mixture [5]+hydrated lime (4 lb.)	1.55	do	None	11	13
17. No. 16+lead arsenate (2 lb.)	1.55	do	Slight	11	11

[1] Stoichiometrical quantities of ferrous sulfate and sodium dimethyl dithiocarbamate were mixed to give ferric dimethyl dithiocarbamate at the rate of 2 pounds per 100 gallons of spray fluid.

[2] In the tests (Nos. 5, 6, 7, 8) of the effect of changing the order of adding ingredients 2 pounds of ferrous sulfate=A; 2 pounds of sodium dimethyl dithiocarbamate=B; 4 pounds of bentonite=C; 1 pint of 40 percent nicotine sulfate solution=D.

[3] As in No. 1, the required quantities of zinc sulfate and sodium dimethyl dithiocarbamate were mixed in water to give zinc dimethyl dithiocarbamate at the rate of 2 pounds per 100 gallons of spray fluid.

[4] As in No. 1, the required quantities of lead acetate and sodium dimethyl dithiocarbamate were mixed in water to give lead dimethyl dithiocarbamate at the rate of 2 pounds per 100 gallons of spray fluid.

[5] A commercial preparation containing 30 percent of lead dimethyl dithiocarbamate in a special clay was used at the rate of 4 pounds with 4 pounds of hydrated lime per 100 gallons of spray fluid.

The tests of the fungicidal properties of the residues indicate in general that, of the metal dialkyl dithiocarbamates studied, those of the dimethyl series appear to offer the most promise while those of the dibutyl series offer the least. Of the diethyl series only the selenium, silver, and mercury salts were fully effective, but the zinc, lead, and copper compounds were partly so (table 2). The addition of lime, as a carrier of the dialkyl dithiocarbamates, or of a combination of lime and of lead arsenate, and lime, as a "safener" for the lead arsenate appeared not to affect the fungicidal properties of the dialkyl dithio-

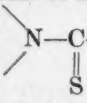
carbamates. The addition of bentonite or of bentonite flocculated by nicotine sulfate likewise failed to reduce the fungicidal efficiency of these compounds. The addition of bentonite flocculated by lime appeared to reduce their fungicidal properties (table 3).

In tests, not recorded in the tables, longer periods of weathering appeared to reduce the fungicidal value of the iron, zinc, and lead dimethyl dithiocarbamates even though considerable quantities of the residue remained on the cover slips. This appeared most pronounced with the iron compound, less with the zinc, and least with the lead.

In the perfusion tests (table 4) where the materials were used without the addition of other chemicals, in general the dimethyl salts were the most effective fungicides, followed in order by those of the diethyl and dibutyl series. This order was maintained with the sodium series.

TABLE 4.—*Tests of toxicity of saturated solutions of some metal dialkyl dithiocarbamates to conidia*

Substituted dithiocarbamates		*Sclerotinia fructicola*		*Glomerella cingulata*	
Metal	Alkyl group	Conidia killed	Perfusion period	Conidia killed	Perfusion period
		Percent	*Hours*	*Percent*	*Hours*
Sodium	Dimethyl	100	2	100	2
	Diethyl	100	22	100	4
	Dibutyl	99+	24	99+	24
Ferric	Dimethyl	100	2	100	2
	Diethyl	48	24	32	24
	Dibutyl	0	24	0	24
Zinc	Dimethyl	100	4	100	4
	Diethyl	0	24	0	24
	Dibutyl	0	24	0	24
Lead	Dimethyl	100	4	100	2
	Diethyl	100	24	100	4
	Dibutyl	20	24	50	24
Copper	Dimethyl	100	6		
		100	2	100	2
	Diethyl	100	22	100	22
	Dibutyl	0	24	0	24
Silver	Dimethyl	100	22	0	24
	Diethyl	100	2	100	2
	Dibutyl	100	22	100	4
Mercury	Dimethyl	100	2	100	2
	Diethyl	100	2	100	2
	Dibutyl	100	2	100	2
Selenium	Diethyl	100	2	100	2

The present study does not indicate the grouping in the metal dialkyl dithiocarbamate molecule that is responsible for either the phytocidal or the fungicidal behavior of the various compounds. Where copper, selenium, mercury, or silver is part of the molecule, it seems certain that these could exercise considerable influence on both properties. Where iron, lead, or zinc is concerned the answer becomes hard to find. As stated previously, Hand (*6*) and Tisdale and Williams (*10*) were of the opinion that all these compounds are of value as fungicides or insecticides because of the presence of the characteristic group  . The phytocidal data appear to indicate that this group, per se, is not responsible for plant injury; the fungicidal data do not clearly indicate that this group, per se, is responsible for the

fungicidal properties. All the compounds possess this grouping, yet many possess no fungicidal properties when used alone or with adjuvants. There is some indication that the fungicidal property may be correlated with solubility, but a few contradictory results obtained with some of the compounds more or less invalidate this theory. This is particularly true of the more soluble dialkyl dithiocarbamates. Among these the fungicidal property was greatest with the methyl compound and least with the butyl, yet all were completely soluble at the concentration used. The data appear to indicate that in addition to the effect, if any, of the characteristic disulfide group, or a byproduct of this group (CS_2), the character of the dialkyl groups may modify the fungicidal property. This was greatest with the dimethyl and least with the dibutyl series.

FIELD TESTS

Experiments for the Control of Apple Scab

Table 5 shows the results of spraying with ferric dimethyl dithiocarbamate at the Missouri station for the control of apple scab and the prevention of fruit russet. Apple scab was well controlled without any noticeable effect on fruit vigor, finish, or color. At the Maryland station ferric and lead dimethyl dithiocarbamates were sprayed on Delicious, Stayman Winesap, Grimes Golden, Golden Delicious, and York Imperial apple varieties, but because of the dry weather in the early part of the season no fruit scab and only a moderate amount of leaf scab developed on the check trees.

At the Maryland station during the early dry warm season both the iron and the lead compound caused a small amount of spot necrosis between the veins of the leaves of all varieties, but this injury was so slight that at the end of the season none could be detected. The spray residues were uniform, weathered well, and did not inferfere with the normal coloring of the fruit of any apple varieties tested. The residues of the lead compounds were the most tenacious. The materials proved rather easy to handle at both stations and caused no harm to the machinery or to the operators. At neither station was russet a factor, and a fine finish developed on all varieties regardless of treatment.

TABLE 5.—*Comparison of control of apple scab and russet by ferric dimethyl dithiocarbamate and by standard fungicides, Mountain Grove, Mo.*

Treatment	Variety	Drops			Harvested fruit			Total crop		
		Total	Scabbed	Russeted	Total	Scabbed	Russeted	Sound	Scabbed	Russeted
		Number	*Number*	*Number*	*Number*	*Number*	*Number*	*Percent*	*Percent*	*Percent*
No fungicide [1]	Rome Beauty	9,596	9,184	<10	2,071	1,917	<10	4.9	95.1	<1
Ferric dimethyl dithiocarbamate mixture+lead arsenate.[2]	do	5,501	216	<10	1,264	31	<10	96.9	3.2	<1
Liquid lime-sulfur; bordeaux mixture; lead arsenate.[3]	do	1,477	14	<10	672	5	<10	99.2	.8	<1
No fungicide [1]	Golden Delicious	1,051	1,050	12	390	389	9	<.1	99.9	1.4
Ferric dimethyl dithiocarbamate mixture+lead arsenate.[2]	do	163	4	2	171	5	8	97.4	2.6	2.9
Liquid lime-sulfur; wettable sulfur, hydrated lime, lead arsenate.[4]	do	188	1	4	278	0	5	99.9	.1	1.9
Lead arsenate, hydrated lime [5]	do	509	276	42	643	397	54	41.6	58.4	8.3

[1] 4 pounds of hydrated lime and 2 pounds of lead arsenate per 100 gallons of spray fluid (3 cover applications).
[2] 3 pounds of ferric dimethyl dithiocarbamate, 4 pounds of hydrated lime, and 2 pounds of lead arsenate per 100 gallons of spray fluid (3 blossom and 4 cover applications).
[3] 2.5 gallons of liquid lime-sulfur to 100 gallons of spray fluid (3 blossom and 1 cover application); 4–6–100 bordeaux mixture (3 cover applications); 2–100 lead arsenate (1 calyx and 4 cover applications).
[4] 2.5 gallons of liquid lime-sulfur per 100 gallons of spray fluid (3 blossom applications); 8 pounds of wettable sulfur, 4 pounds of hydrated lime, and 2 pounds of lead arsenate to 100 gallons of spray fluid (1 calyx and 4 cover applications).
[5] 4 pounds of hydrated lime and 2 pounds of lead arsenate to 100 gallons of spray fluid (1 calyx and cover applications).

EXPERIMENT FOR THE CONTROL OF PEACH SCAB AND BROWN ROT

Table 6 shows the results of applications of ferric dimethyl dithiocarbamate to peach varieties at the Maryland station. The season was favorable for peach scab, since frequent rains and moderate temperatures occurred during most of the growing season. By harvesttime the fruits of the check trees of the Carman and Elberta varieties were often cracked from the disease. The late season was somewhat dry, and brown rot was not the menace that it usually is at the Maryland station. Only a trace of scab and very little brown rot developed on the sprayed Alexander and Carman varieties. Only a trace of brown rot and 9.2 percent of scab, all of a light character and insufficient to cause a loss of grade, developed on the Elberta variety. The fruit developed a fine finish in all cases. The material, however, had a physiological effect upon the ripening processes that delayed maturity of all varieties from 7 to 10 days and likewise interfered somewhat with the development of color. The material caused no noticeable blemishes on the fruit of the various varieties, but on all varieties certain leaf injuries occurred throughout the season. After the first two applications, in which zinc sulfate was combined with the mixture to prevent injury by the lead arsenate, a few necrotic spots developed between the veins of the younger leaves. These were noticeable several days after the applications but soon became hard to find as new foliage developed. When the later cover applications were made without zinc sulfate and lead arsenate, this type of injury developed in increasing amounts. It appeared that the material had become changed as it aged in the warehouse. In the last application, the injury was very severe, but it resulted in little defoliation.

TABLE 6.—*Control of peach scab and brown rot by ferric dimethyl dithiocarbamate. Beltsville, Md.*

Treatment	Variety	Fruit counted	Scab		Fruit affected by brown rot	Fruit affected by worms
			Fruit affected	Severity on affected fruit		
		Number	*Percent*		*Percent*	*Percent*
Ferric dimethyl dithiocarbamate mixture.[1]	Alexander	467	<1.0	Light	<1.0	16.7
No treatment	do	610	89.9	Heavy	3.9	43.0
Ferric dimethyl dithiocarbamate mixture.[1]	Carman	319	<1.0	Light	5.0	16.8
No treatment	do	666	100	Heavy	21.5	36.9
Ferric dimethyl dithiocarbamate mixture.[1]	Elberta	1,432	9.2	Light	<1.0	23.1
No treatment	do	1,231	100	Heavy	40.5	68.3

[1] 2 pounds of ferric dimethyl dithiocarbamate and 8 pounds of hydrated lime per 100 gallons of spray fluid (5 applications); 2 pounds of lead arsenate and 2 pounds of zinc sulfate added to shuck and first cover, but not to second, third, and fourth cover, applications.

EXPERIMENTS FOR THE CONTROL OF CHERRY LEAF SPOT

Table 7 shows the results of applications of ferric dimethyl dithiocarbamate to the Montmorency variety of cherry at Beltsville, Md. The early part of the season was not particularly favorable for the development of cherry leaf spot, but considerable leaf spot developed as the season advanced. At harvesttime development from tree to

tree was not uniform, but as the season advanced the disease spread rapidly through the planting, subjecting the materials to a thorough test. Many of the trees were bare at the beginning of October, some weeks before the advent of frost. No injury resulted from the treatments, but leaf spot was not controlled.

TABLE 7.—*Comparison of control of leaf spot of Montmorency cherries by ferric dimethyl dithiocarbamate and by copper phosphate, Beltsville, Md.*

Treatment [1]	Trees	Average size of fruit at harvest [2]	Leaf infection (average of all trees in plot) on—		Leaf fall (average of all trees in plot) on—	
			Aug. 30	Sept. 26	Aug. 30	Sept. 26
Ferric dimethyl dithiocarbamate mixture [3]	*Number* 8	*Grams* 4.31	*Percent* 78.0	*Percent* 100.0	*Percent* 10.0	*Percent* 74.5
Copper phosphate mixture [4]	9	3.79	.45	13.3	0	2.0
No treatment	3	4.06	100.0	100.0	80.0	96.0

[1] 1 petal-fall and 2 cover applications.
[2] About 2 pounds of fruit was collected from each tree by harvesting the fruit around the tree at breast height.
[3] 2 pounds of ferric dimethyl dithiocarbamate, 8 pounds of lime, and 2 pounds of lead arsenate per 100 gallons of spray fluid at petal fall; same without lead arsenate in 2 cover applications.
[4] 2 pounds of copper phosphate, 8 pounds of lime, and 2 pounds of lead arsenate per 100 gallons of spray fluid at petal fall; same without lead arsenate in 2 cover applications.

SUMMARY

Results of experiments to determine the fungicidal and phytocidal properties of some metal dialkyl dithiocarbamates, including the sodium, ferric, lead, zinc, copper, silver, and mercury dimethyl, diethyl, and dibutyl dithiocarbamates and selenium diethyl dithiocarbamate, are reported.

Most of the heavy metal dialkyl dithiocarbamates were produced in the laboratories of the United States Horticultural Station, Beltsville, Md., by reacting solutions of commercial sodium dialkyl salts with solutions of suitable heavy metal salts.

The sodium salts have a basic reaction while the salts of the heavy metals are acid or neutral. The soluble sodium salts were phytocidal. The selenium, copper, and mercury salts were all phytocidal to all the various plants used, while those of iron, zinc, and silver varied in this respect. The lead salts caused no injury to any of the plants, while the zinc salts caused more or less injury to peach and bean and the dimethyl salt of iron caused slight injury to peach. Apparently iron and zinc salts become changed by weathering.

The dimethyl derivatives appeared in general to possess the greatest fungicidal value. The dibutyl derivatives in general possessed the least. The iron, lead, and zinc dimethyl derivatives appeared to offer the greatest promise since these caused the least plant injury. The lead salts appear the most promising from all standpoints.

Preliminary tests indicated that the iron, zinc, and lead derivatives can be made up in the spray tank by mixing stoichiometrical equivalents of the reacting salts. Such an operation results in a product that remains in suspension and has superior sticking qualities. The zinc and iron mixtures of this type caused slight injuries to peach, while none caused injury to apple.

All of the metal dialkyl dithiocarbamates were compatible with hydrated lime and lead arsenate. Special tests with the iron dimethyl

dithiocarbamates indicated that this metal derivative retained its fungidicidal efficiency where combined with bentonite or nicotine sulfate and bentonite but not with bentonite flocculated with lime.

Field tests were conducted in Maryland and Missouri on a small scale with ferric dimethyl dithiocarbamate for the control of apple scab. The product used was a commercial sample. In spite of the fact that there was little scab at the Maryland station the results were satisfactory, and the material showed enough promise to justify continuing the tests. The material controlled scab and brown rot on peach in Maryland without causing fruit injury, but it caused leaf spotting which became progressively greater as the material on the leaves aged. On cherry, no injury occurred, but leaf spot was not controlled.

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